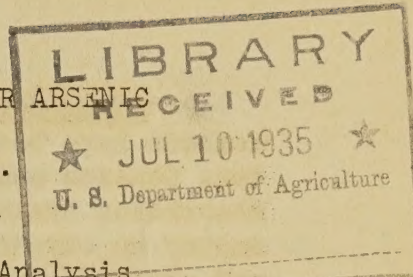


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MEMORANDUM FOR PROSPECTIVE COLLABORATORS ON METHODS FOR ARSENIC

C. R. Gross, Associate Referee, June 26, 1935.



The last revision of the A. O. A. C. Methods of Analysis occurred in 1930 at which time the Gutzeit method was revised and adopted as a tentative method for the determination of arsenic in foods and plants (1). Since that revision was made, several writers have questioned the accuracy of the method for analyzing certain products such as shrimp, oils and tobacco (2), (3), (4), and other writers (5) have questioned its general accuracy due to losses of arsenic during acid digestion.

Mr. H. J. Wichmann, General Referee on Metals in Foods, in the arsenic section of his recently published "Report on Metals in Foods" (6), a copy of which is here appended, has given a concise summary of our present problems in arsenic analysis. He stresses the fact that greater attention should be given to methods for preparation of the sample and isolation of arsenic to remove interferences in order that impossible accomplishments are not required for the Gutzeit or other methods of analysis in particular problems. He recommends that the general problem be studied through the medium of a "flow sheet" which segregates the methods of preparation, isolation and determination and shows the combinations of those steps of analysis which are practicable for use.

Your Associate Referee on methods for arsenic has prepared the appended flow sheet for such a study. It would be both impractical and impossible to make a study this year of all the steps and combinations of steps which the flow sheet indicates. Seven of the more promising steps in analysis have been selected for study. These are indicated by number on the flow sheet. Your interest and assistance in conducting the studies planned is solicited as it is important that as much work be done as possible along these lines and that the information be available for discussion at the fall meeting of the A.O.A.C., following which a new revision of the Methods of Analysis will be made. It is accordingly suggested that you read over the general description of the different lines of study planned and communicate with your Associate Referee concerning those lines on which you would be interested in affording assistance. At that time you will be sent specific directions covering the lines of study selected, as well as test samples and solutions.

The test samples and solutions will be drawn from a variety of materials, both refractory and non-refractory towards ordinary acid digestion, and containing natural or added arsenic, or both. By using samples from a common source, the results of different methods by the same or different investigators can be compared.

Methods of Sample Preparation

Study No. 1 - Dry Ashing in Inclosed Systems: Two such methods have been described recently in the literature, that of Remington, Coulson and von Kolnitz (3) who use an inclosed torch with an absorption train, and that of Carey, Blodgett and Satterlee (5) who employ an oxygen bomb combustion chamber with suitable precipitating and absorption chambers. Collaborative studies comparing results of analyses using these or similar systems with analyses on other samples from the same source digested by the A.O.A.C. method will be appreciated by the Associate Referee. In these tests the arsenic in the prepared solutions will be determined by the Gutzeit method, preceded if necessary by the method of phosphate precipitation used by Gross (4) for separation of arsenic from interfering substances in the analysis of tobacco.

Study No. 2 - Dry Ashing with Fixatives: Mr. Wichmann has suggested the trial of aluminum and/or magnesium nitrate and nitric acid, using a technic similar to that employed for determining total sulfur in fruits and fruit products (7). If such a method could be used on a variety of products refractory towards digestion, it would have the advantage of eliminating the specialized equipment necessary for dry oxidation in inclosed systems. Hertzog (8) has successfully used a mixture of sodium carbonate, magnesium oxide and potassium nitrate for the dry ignition of coal. He took up the residue with sulfuric acid and analyzed for arsenic by the Gutzeit method.

Preliminary tests are being made by the Associate Referee on various modifications of the Wichmann and the Hertzog technics. Any promising leads will be transmitted to collaborators interested in this phase of the subject.

Methods of Isolation of Arsenic

Study No. 3 - Arsine Evolution: This step does not refer to the Gutzeit evolution of arsine but to the method of C. R. Smith (9) whereby the arsine is isolated by distillation into mercuric chloride solution and is evaluated by iodine titration. Taber (10), (11) modified this procedure by substituting a larger generator flask to accommodate several hundred cc. of sample solution and by attaching a condenser so that the solution could be heated to secure proper reduction of the arsenic and a vigorous ebullition of the hydrogen and arsine gases. Taber's object was to obtain a method which could be applied directly on the 300-500 cc. of solution obtained by stripping the arsenic from fruits in routine spray residue analysis with boiling dilute solutions of an acid or alkali.

Taber found that the results were satisfactory when he used pure solutions of arsenic but where stripping solutions containing organic matter were used, the results were sometimes low. It has been the experience of the Associate Referee and others (12), (13) that this method of isolation cannot always be depended upon where digested solutions from plant materials are concerned.

A promising modification for securing complete distillation of the arsenic has been offered by Lachele (14) who passes a current of an inert gas, such as nitrogen or hydrogen, through the solution in the generator flask. This circulates the solution, increasing the chances that all parts of it will be exposed to the action of the nascent hydrogen produced on the surface of the zinc and aids in sweeping the evolved arsine through the rest of the apparatus. About 250 cc. of solution including reagents is concerned in Lachele's technic and he finds that the arsine is usually completely evolved in fifteen minutes.

Lachele evaluates the arsenic by the comparison of the densities of the stains produced on mercuric bromide paper discs. This method will be tried by the Associate Referee together with any collaborators who are interested, but the main study in this case will be to modify Taber's technic by employing Lachele's method of gas flow. Evaluation will be by the method of absorption in mercuric chloride and iodine titration and comparisons will be made with results obtained by other methods of analysis.

Study No. 4 - Arsenic Trichloride Distillation: A satisfactory technic for acid digestion followed by arsenic trichloride distillation and bromate titration has been worked out by Jones (15) and was adopted as a tentative method for fresh fruits by the A.O.A.C. in 1933. Jones used ferrous sulfate and sodium bromide as reducing agents for the arsenic trichloride distillation step. In 1934 the Association approved the amendment to substitute hydrazine sulfate for ferrous sulfate in order to facilitate making lead determinations on the same solution.

The latter technic has sometimes occasioned high bromate titrations due to the distillation of sulfur dioxide produced by the action of the hydrazine sulfate on the sulfuric acid used for digestion of the sample. Collaboration is desired to develop a set of conditions which will obviate the danger of sulfur dioxide interference.

Isolation and Determination of Arsenic

Study No. 5 - Increased Range of Arsenic Standards in Gutzeit Method: The present A.O.A.C. method specifies standards ranging from 5 to 30 gamma of arsenic trioxide. It would be very convenient to be able to employ a wider range than this. Gross (16) has reported from unpublished data by H. Heidenhain that the latter, mainly through the expedient of increasing the volume in the evolution bottle to 60 cc. in place of 40 cc. has successfully employed standards up to 100 gamma. Limited observations by Gross have verified that this may be satisfactorily accomplished.

Before definite recommendations can be made, however, it will be necessary to establish the optimum combination of conditions of evolution, particularly with respect to the quantity and type of zinc, the quantity of acid and the volume of the solution. Collaboration is invited on this phase of the subject.

Study No. 6 - Molybdate Colorimetric Method: This method is based upon the blue color developed when arsenates or phosphates are acted upon by a reducing agent in an acid mixture in the presence of molybdic acid. Various methods have been devised for developing the blue arseno-molybdate colors, but only two, the Zinzadze (17) and the Kuttner-Cohen (18), are sufficiently sensitive for determination of arsenic in foods and plants. These two methods differ in various details, principal of which is the type of reducing agent used. Zinzadze's completed reducing agent is made by mixing sulfuric acid solutions of MoO_3 and powdered molybdenum. Kuttner and Cohen used a sulfuric acid solution of Na_2MoO_4 and add stannous chloride to develop the color.

Methods for employing the molybdate colorimetric method for analysis of foods and plants have been brought forth by Deemer and Schricker (12), who use the Zinzadze method of color development and Fitelson (13) who employs the Kuttner-Cohen method. Deemer and Schricker use acid digestion followed by arsenic trichloride distillation to isolate the arsenic for colorimetric analysis. Fitelson uses a method of precipitating the arsenic as the trisulfide along with sulfur as a coprecipitant.

Both the Deemer-Schricker and the Fitelson methods of isolation and colorimetric determinations have their commendable and objectionable features and it will be the object of collaborative work to study both methods and devise a new method based upon the best qualities of both.

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Preparation of Sample

ISOLATION OF ARSENIC

Determination
of Arsenic

**Cerulo-Molybdate
Colorimetric**

Bromate Titration

Iodine Titration

HgBr₂ Paper
Strips
(Gutzeit)

HgBr₂ Paper
Discs
(Lachelo)

